

Chemistry at Extreme Conditions

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*This article was submitted to
40th European High-Pressure Research Group Meeting
Edinburgh, Scotland
September 4-7, 2002*

August 8, 2002

U.S. Department of Energy

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CHEMISTRY AT EXTREME CONDITIONS

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We present equation of state results from impulsively stimulated light scattering (ISLS) experiments conducted in diamond anvil cells on pure supercritical fluids. We have made measurements on fluid H₂O (water), and CH₃OH (methanol). Sound speeds measured through ISLS have allowed us to refine existing potential models used in the exponential-6 (EXP-6) detonation product library [Fried, L. E., and Howard, W. M., *J. Chem. Phys.* **109** (17): 7338-7348 (1998).]. The refined models allow us to more accurately assess the chemical composition at the Chapman-Jouget (C-J) state of common energetic materials. We predict that water is present in appreciable quantities at the C-J state of energetic materials HMX, RDX, and nitro methane.

Keywords: Equation of state; Super critical fluids; Water; Methanol; CHEETAH; ISLS

1 INTRODUCTION

Experiments at extreme conditions of pressure and/or temperature provide insight into a realm of chemical and material properties that are significantly different from those encountered under ambient conditions. Such studies extend and test the theoretical framework which permits progress from properties at the atomic and molecular level to macroscopic behavior, and constitute a potential source of novel materials and new tools for chemical transformation and are important adjuncts to progress in other disciplines. There is no question that an improved general knowledge of electronic, physical, and chemical behavior of relevant constituent materials at high density is required, for example, for a less fragmented description of the planetary environments and also of processes that precede and direct detonation. The purpose of the work described in this paper is to ultimately develop a quantitative model of material properties and states under chemically and physically extreme conditions not currently achievable in the laboratory setting.

Knowledge of an effective interatomic potential function underlies any effort to predict or rationalize the properties of solids and liquids. Particularly in systems associated with experimentally difficult temperatures or pressures, such as those that prevail in detonations, the deep interiors of the Earth, and giant planets, models based on intermolecular potentials seems at present the most promising predictive resource. While there exists an extensive body of experimental techniques and experience on computational methods appropriate to ambient conditions, the regime of strong repulsive interactions at very high densities has not been as extensively investigated. The experiments discussed here are aimed both at enlarging the family of properties conveniently measured at high pressure and, principally, at providing the data appropriate to a critical test of the theory of the internuclear potential in simple substances at high density.

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2 EXPERIMENTS

The optical technique Impulsive Stimulated Light Scattering (ISLS) is discussed in general in Refs. [1-2] and specifically in the context of the diamond anvil cell (DAC) in Refs. [3-5]. Briefly, two successive "excitation" pulses, (30 μJ , 60 μm diameter, ~ 100 ps duration) are selected from the output train of a Q-switched (500 Hz), mode-locked Nd:YAG laser and recombined in the sample at an angle 2θ , but otherwise coincident in space and time. Interference establishes a periodic distribution of intensity and, in a sample that absorbs in the near infrared, a (spatially) periodic variation in the temperature and pressure ensues. The coupling between laser light and the excited material modes is such that the local temperature rise remains "impulsive." The associated thermal pressure launches counter-propagating acoustic waves. The acoustic wavelength, d , in this case equal to the period of the optical grating, may be expressed in terms of the excitation wavelength, $\lambda_E = 1.064$ μm , and θ as $d = \lambda_E / 2 \sin \theta$.

In a fluid sample one longitudinal wave is excited. The impulsively excited acoustic wave induces a temporally and spatially periodic variation in the index of refraction of the sample. A third pulse (~ 1 μJ , 20 μm diameter, ~ 80 ps duration) selected from the same Q-switched envelope as the excitation pulses is frequency doubled ($\lambda_P = 0.532$ μm) and delayed by a combination of time of flight and mode lock pulse selection to generate the "probe." Observation of the intensity of the Bragg scattering of the probe, by the acoustic or thermoacoustic grating, as a function of probe delay serves to determine the frequency (ν), and hence the adiabatic velocity ($c = d\nu$) of the acoustic waves. In practice, grating spacings are determined by making the same measurement on a piece of glass with a known speed of sound and which gives a strong, stable signal suitable for a calibrant. The velocity is typically determined with a precision of $< \pm 0.2\%$.

Pressure determinations were made by monitoring the wavelength of the fluorescence (excited by a He-Cd laser or by the 488-nm Ar^+ laser line) of ruby chips or Raman of carbon 13 chips, which surround or are embedded in the sample. Rubies after grinding to tens of microns have residual strains which are often large enough to offset pressure measurements by ~ 0.05 GPa, and occasionally as much as 0.2 GPa. Annealing at $\sim 1000^\circ\text{C}$ for several hours decreases both the magnitude and frequency of these deviations yet it is still common to find rubies which differ reproducibly by the equivalent of 0.02 GPa. The most precise work completed has been on the melting curve of O_2 , in which the relative wavelengths of rubies were recorded at 0 GPa and the high-pressure results corrected by the same amounts. The reference rubies at 1 atm were kept in the same temperature controlled housing as were the samples, because wavelength shifts equivalent to 0.01 GPa are generated by temperature differences of 0.5°C and in order to match as closely as possible the two spectral line shapes. With hydrostatic samples one can measure pressures using ruby with a precision of slightly better than 0.01 GPa.

3 COMPUTATIONS

CHEETAH is a thermochemical code that is used to predict extreme condition reaction products and energy release from C,H,N,O molecules. CHEETAH solves thermodynamic equations between product species to find chemical equilibrium for a given pressure and temperature. Chapman-Jouget (C-J) theory says that the detonation point is a state in thermodynamic and chemical equilibrium, so CHEETAH can predict the properties of this state. From these properties and elementary detonation theory the detonation velocity and other performance indicators are computed.

Thermodynamic equilibrium is found by balancing chemical potentials, where the chemical potentials of condensed species are just functions of pressure and temperature, while the potentials of gaseous species also depend on concentrations. In order to solve for the chemical potentials, it is necessary to know the pressure-volume relations for species that are important products in detonation. Moreover, it is necessary to know these relations at the high pressures and temperatures that typically characterize the CJ state. Thus, there is a need for improved high-pressure equations of state for fluids, particularly for molecular fluid mixtures. The exponential-6 (EXP-6) potential model defines the energy of interaction of a classical fluid composed of identical spherical particles. This model has been used with considerable success to describe the equation of state of many materials over a wide range of pressure and temperature [6]. The EXP-6 potential has also proved successful in modeling chemical equilibrium at the high pressures and temperatures characteristic of Jovian planet interiors and detonation processes. However, in order to calibrate the parameters for such models, it is necessary to have experimental data for molecules and mixtures of molecular species at high temperature and pressure. Static compression data, as well as sound speed measurements, provide important data for these models.

4 SOUND VELOCITIES OF SUPERCRITICAL FLUIDS

Measurements were performed on the sound speed of H_2O along six isotherms. A comparison between measured sound speeds along 200°C 300°C, and 400°C isotherms and the present two-species model is given in Figure 1. Results are shown in Table I. The H_2O sound speed data allowed us to refine the EXP-6 potential model used in CHEETAH. EXP-6 refined parameters for species considered here are given in Table II. The model is consistent with static sound speed, compression, and shock Hugoniot measurements.

The sound velocity of pure methanol (MeOH) was measured along a 250°C isotherm up to 3.9 GPa. After each data point was taken the sample was cooled and the velocity was again measured and compared to previous measurements of uncooked MeOH [10]. The measured sound speeds for MeOH are given in Table III. A comparison of ISLS experimental data and CHEETAH computational results are given in Figure 1. The EXP-6 potential model used was based on the shock Hugoniot of methanol. The ~3% difference between data sets shows the utility of CHEETAH and the consistency between static and dynamic equation of state measurements.

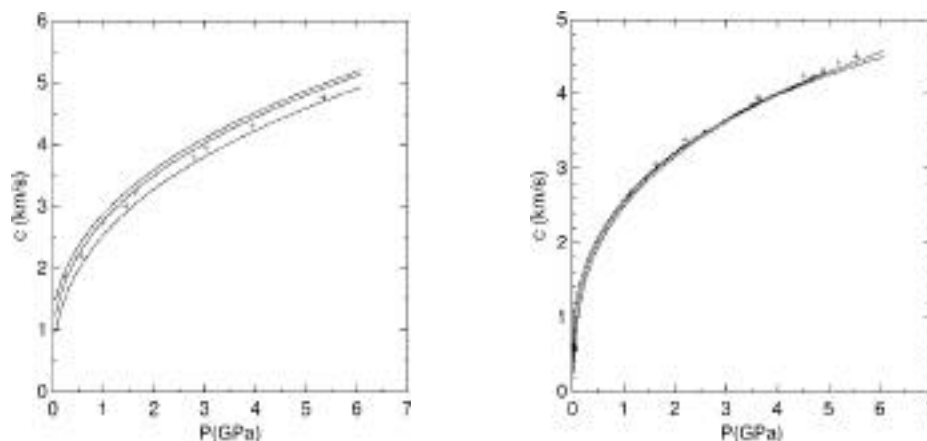


Figure 1. Measured velocities (crosses) for CH_3OH (left) and H_2O (right) compared to calculations.

Table I. Measured Velocities for water.

P(GPa)	T(C)	c(km/s)
0.86	100	2.612
1.105	100	2.788
1.410	100	3.028
1.600	100	3.161
2.150	100	3.471
1.00	115	2.734
1.44	115	3.065
1.65	115	3.182
2.19	115	3.465
2.29	115	3.516
0.88	150	2.631
2.314	150	3.541
0.500	200	2.254
0.937	200	2.685
1.090	200	2.800
2.770	200	3.706
3.060	200	3.823
3.230	200	3.885
3.590	200	4.020
1.621	300	3.059
2.195	300	3.372
3.612	300	3.951
4.513	300	4.246
5.206	300	4.424
5.543	300	4.517
1.120	400	2.660
1.130	400	2.660
1.417	400	2.844
2.179	400	3.304
2.605	400	3.500
3.513	400	3.857
3.675	400	3.923
4.689	400	4.234
4.893	400	4.310
4.903	400	4.310

Table II: Heat of formation (H0: kJ/mol), standard entropy (s0: kJ/mol-k), exp-6 potential minimum (rm: Å), well depth (e: K) and steepness parameter (a) for species studied in this work.

Species	H0	S0	rm	e	a
CH2O	-116	0.219	3.72	350	13.0
CH2Oa	-119	0.217	5.64	350	13.0
CH3OH	-201	0.240	4.24	507	13.0
H2O	-242	0.189	3.43	397	10.7
H2Oa	-288	0.093	3.21	397	10.7

Table III. Measured 250°C Velocities for methanol

P(GPa)	c(km/s)
0.561	2.194
0.987	2.720
1.424	3.000
1.633	3.219
2.640	3.771
3.160	4.023
3.890	4.255

Acknowledgements

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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